A State Between Liquid and Crystal: Locally Crystalline but with the Structure Factor of a Liquid

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We are familiar with large highly-ordered single crystals, such as those used in the semiconductor industry. There the crystalline ordering in the silicon crystals extends for billions and more lattice spacings. As a result, X-ray diffraction (XRD) patterns of these crystals have sharp Bragg peaks. We are also familiar with liquids, where the molecules have a local structure that is very different to that in a crystal. In addition, in liquids there is only ordering over a few molecular diameters, and so they do not have Bragg peaks. But there are materials, where the situation is much less clear. Many of these materials are referred to as amorphous.

For example, the structure of amorphous silicon is controversial. There is debate[1–3] over whether it possesses some crystalline ordering of the sort variously referred to as paracrystalline order, nanocrystalline order or medium-range crystalline order, or whether it has no crystalline ordering. We do not know if locally, silicon atoms are arranged in the structure of a liquid, or whether they are in tiny crystals only a few silicon atoms across. There are other systems at the borderline between liquid and crystal. The mineral ferrihydrite can be classified as crystalline (this is called six-line ferrihydrite), or as amorphous (this is called two-line ferrihydrite).[4–6]

The structures of Amorphous Calcium Carbonate (ACC),[7–16] Amorphous Calcium Phosphate (ACP),[17] and Amorphous Calcium Sulphate (ACS)[18–20] are also poorly understood. The properties of ACC clearly depend on how it is prepared,[9,21–24] and Gebauer *et al.*[23] refer to 'proto-vaterite' and 'proto-calcite' forms of ACC, which although amorphous have NMR and EXAFS spectra that have (broadened) features in common with vaterite, and with calcite, respectively. Vaterite and calcite are two of the crystal polymorphs of calcium carbonate.

Experimental data such as XRD can clearly distinguish between large single crystals and liquids, but as we have known since Scherrer's work a hundred years ago,[25] as the size of crystallites decreases, the width of the Bragg peaks in the structure factor $S(k)$ increases. Finite size effects give a peak width $\Delta k \approx k/n$, for a crystallite n lattice spacings across. For $n \lesssim 10$, the peak is so broad that it is essentially as broad as features in the $S(k)$'s of liquids, and so XRD is not be able to distinguish between a liquid or glass, and a state made of very small crystallites. In computer simulations we can circumvent the problem this causes in identifying a state, as there we know the exact positions of all molecules, in real space, and so have much more information than is contained in an XRD pattern.

Here we use computer simulation to study crystallisation in microscopic detail, in a simple model: the Gaussian Core Model (GCM).[26] In the GCM, molecules interact via the spherically symmetric potential $v(r) = \varepsilon \exp[-r^2/\sigma^2]$, where the parameters ε and σ have dimensions of energy and length, respectively. This is a simple model with three competing polymorphs: body-centred cubic (bcc), face-centred cubic (fcc) and hexagonal close-packed (hcp). The GCM phase diagram has regions where the bcc crystal phase is stable, and others where the fcc crystal phase is stable.[27,28]

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All our results are at the state point $T = 0.002\varepsilon/k_B$, $P = 0.0055\varepsilon/\sigma^3$, where the fcc phase is stable.[27,28] The simulations are *NPT* Metropolis MC algorithm. In these simulations, our unit of time, τ, is a single MC cycle, which consists of one attempted displacement move per molecule and one attempted box-size move.[29]
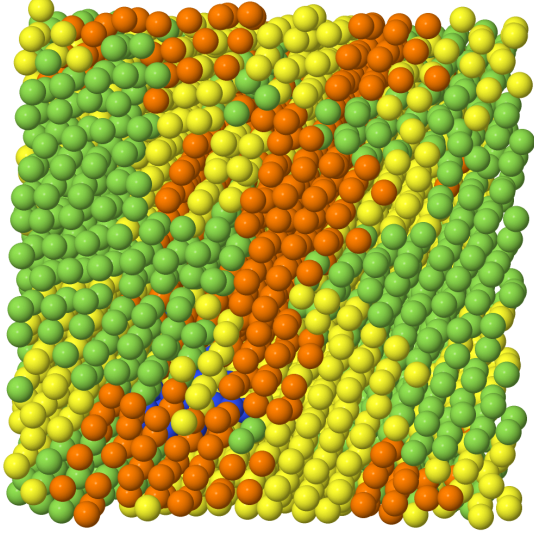

Figure 1: An example amorphous configuration. Here, and in all subsequent figures, molecules in an fcc-like local environment are yellow, bcc-like are green, hcp-like are orange, and liquid-like are blue. It is typical of the results of ≈ 150 independent runs. Its composition is 36% fcc, 42% bcc, 2% hcp and 1% liquid. It is configuration number 5 of Table S1.

Starting from the liquid phase, we see nucleation and growth of a state in which $> 95\%$ of the molecules are in crystalline environments. This state forms via the conventional nucleation then growth kinetics of a first-order transition, see Mithen *et al.*[30] for further details.

In Figure 1, we show simulation snapshots of two configurations of this state. Note that although almost all the molecules have crystallised in the sense that they are now in locally crystalline not liquid-like environments, they are in all three polymorphs. Movies *video1.mp4* and *video2.mp4* are rotating animations of these configurations. In these animations, planes of all three crystal polymorphs are clearly visible.

To characterise crystallinity, we use the order parameters introduced by Lechner and Dellago.[31] By taking into account the first and second shells of

nearest neighbours of a molecule, these order parameters allow each molecule to be classified as being in fcc-like, hcp-like, bcc-like, or liquid-like local environments. Further details on how these order parameters are calculated are in the supplemental information, together with the distributions of values they take in this state. We compare these values to those in the bulk liquid and crystal polymorphs, and find that the local crystalline ordering is on average weaker than in the bulk crystals, but that the local structure has clearly changed qualitatively from that in the liquid.
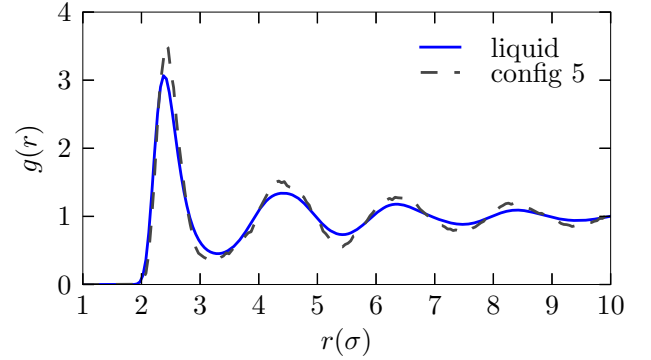
(a)
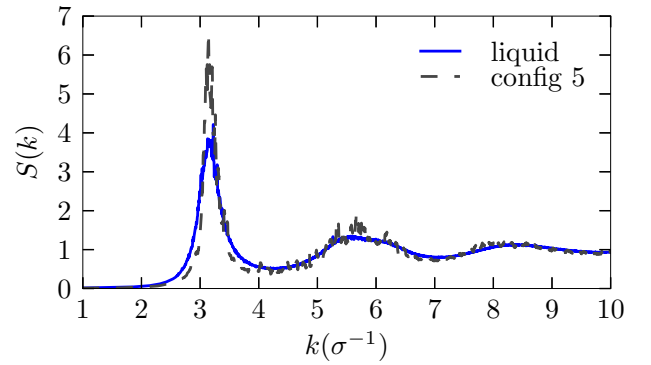
(b)

Figure 2: The $g(r)$ and $S(k)$'s of the state in Figure 1 compared with the $g(r)$ and $S(k)$ in the liquid state.

The structure factors, $S(k)$, and pair distribution functions, $g(r)$, for the two configurations in Figure 1 are shown in Figure 2. The $S(k)$'s and $g(r)$'s are both liquid-like. If we compare the $S(k)$ with that in the liquid, we see that it is very similar, except that the first peak is approximately 50% higher, and a little narrower.

We measured the diffusion coefficient D in the

state, and found it to be much lower than in the liquid, see Supplementary Information. As the state has a liquid-like $S(k)$ but slow dynamics, we refer to the state as amorphous. However, as almost all the molecules in this state are in local environments that are characteristic of one of the three crystalline polymorphs, the state could also be called paracrystalline or nanocrystalline, or be said to have medium-range crystalline order. By exploiting the fact that we have the exact positions in real space for all molecules (unlike in experiment) we have proven that paracrystalline/nanocrystalline/medium-range-crystalline order is consistent with a liquid-like $S(k)$ and $g(r)$.

Our amorphous state is not the equilibrium state, that is the fcc crystal; the bcc crystal is also more stable than the amorphous state. Thus we expected our amorphous state to eventually crystallise into a single crystal of fcc, or possibly into the metastable bcc state. Note that this process is very different from crystallisation from the liquid phase, as domains of the final crystal already exist, and so crystallisation here is growth of one polymorph at the expense of the other.

Although the amorphous state can persist over very long simulation runs without crystallising, we have observed crystallisation from this state. We have observed both crystallisation into the fcc polymorph, see the results in Figure 3, and into the bcc polymorph, see Figure 4. After crystallisation, $S(k)$ has the sharp peaks characteristic of either fcc or bcc crystals, see Figures 3(f) and 4(f). Figures 3(g) and 4(g) show how the polymorph fractions evolve in time. Note that the two amorphous states are formed at the same pressure and temperature, but go on to form crystals of different polymorphs.

To study crystallization from the amorphous state quantitatively, we chose nine configurations, and evolved each one in 200 independent simulation runs. Each run was of up to 3×10^6 MC cycles. Of these nine configurations, seven always crystallised into the same polymorph; this was fcc in four cases, and bcc in three cases. So these amorphous configurations are strongly biased towards to forming a specific polymorph. But they are biased towards different polymorphs. On the other hand, the state of Figure 1 formed a fcc crystal in 102 runs, the bcc crystal 77 times, and did
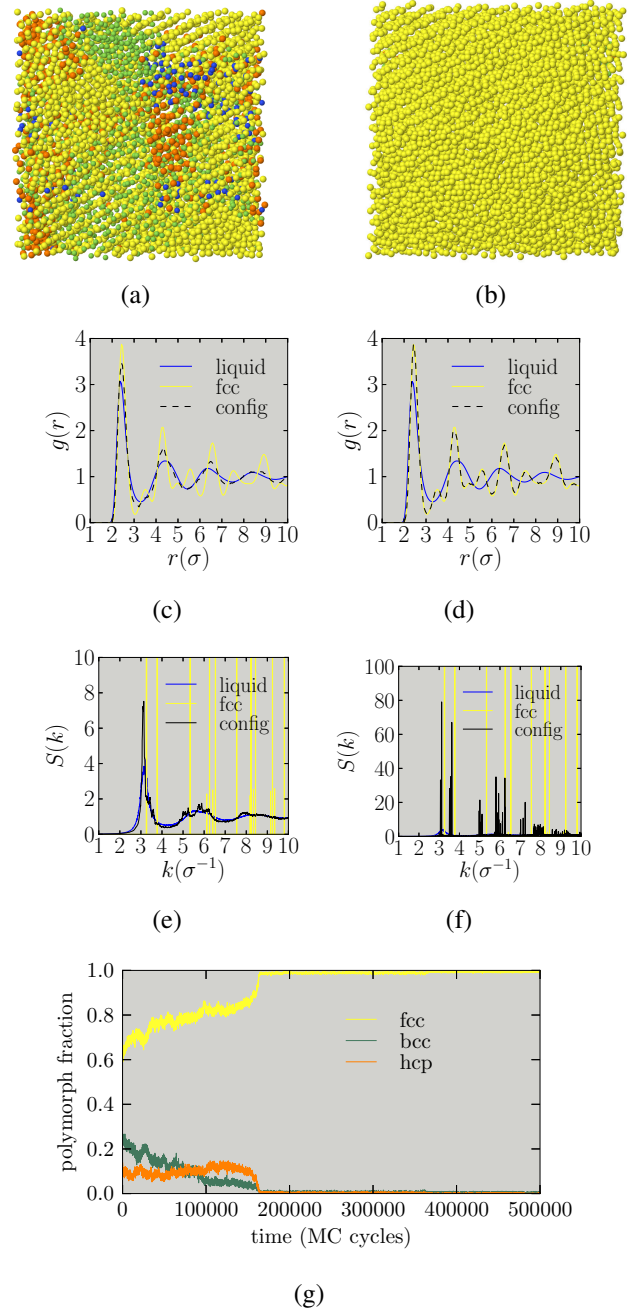

(a) (b)

(c) (d)

(e) (f)

(g)

Figure 3: Typical example of crystallization of the amorphous state into the fcc polymorph. The initial and final configurations are shown in (a) and (b), respectively. (c) and (e) are the $g(r)$ and $S(k)$ of the initial configuration, and (d) and (f) are the $g(r)$ and $S(k)$ of the final configuration. In (c) to (f) we also show results for the liquid and for the fcc crystal, to provide comparisons. (g) is the fraction of the system in each polymorph, as a function of time. In the initial state, 61% of molecules are in an fcc-like environment, 24% are bcc-like, and 12% are hcp-like. This is the configuration number 1 of Table S1, and it crystallises into the fcc polymorph 200 times out of 200.

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not crystallise in the remaining 21 runs. In summary, most but not all (see Table S1) of the nine configurations are already committed to form one of fcc or bcc.

We looked for features of the amorphous state that could predict which polymorph would form. We looked at four things: 1) the $S(k)$ and $g(r)$, 2) the numbers of molecules in the three polymorphs, 3) sizes of clusters of these polymorphs, and 4) average values of the Lechner-Dellago order parameters.

Both the $S(k)$'s and $g(r)$'s in the two states are very similar, compare Figure 3(e) with Figure 4(e), and Figure 3(c) with Figure 4(c). They do not allow us to predict which polymorph will form.

In almost all cases a large majority of the molecules of a given polymorph are in a single connected cluster (Table S2). Thus 2) and 3) give essentially the same information. There is a tendency for the polymorph with the largest number of molecules (and largest cluster) to be the one the forms upon crystallisation. Of the seven systems that always crystallised into the same polymorph, six of them formed a crystal of the polymorph present in the largest amount (Table S2). But one did not. So the polymorph present in the largest amount is only partially predictive of the crystal polymorph that will form.

The situation is similar for the average values of the Lechner-Dellago order parameters. We use the value of the $\bar{w}_6$ Lechner-Dellago order parameter to discriminate between the bcc and close-packed polymorphs. $\bar{w}_6$ is negative in the bulk fcc crystal, and positive in the bulk bcc crystal. Here in six out of the seven configurations that always crystallised into the same polymorph, $\bar{w}_6$ had the same sign in the configuration as in the polymorph that formed, but not in one configuration (Table S1). For one configuration (number 3 of Tables S1 and S2) both $\bar{w}_6$ and the largest polymorph fail to predict the polymorph the forms.

So, to summarise, a majority (7/9) of realisations of the amorphous state are almost completely committed to forming either the fcc or the bcc polymorph as soon as they have formed, while the remainder can go on to crystallise into either polymorph. But surprisingly, even though we know exactly where every molecule is, we do not have an always-reliable method to predict which one will

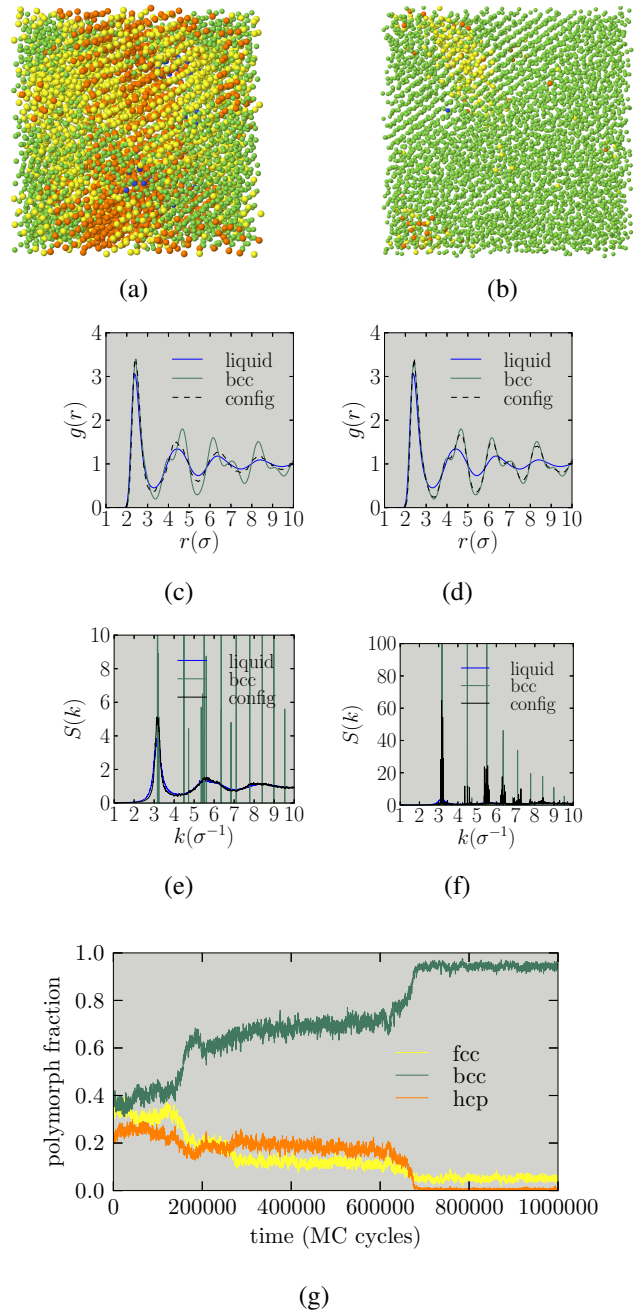(a)　　　　　　　　　(b)

(c)　　　　　　　　　(d)

(e)　　　　　　　　　(f)

(g)

Figure 4: Typical example of crystallization of the amorphous state into the bcc polymorph. The initial and final configurations are shown in (a) and (b), respectively. (c) and (e) are the $g(r)$ and $S(k)$ of the initial configuration, and (d) and (f) are the $g(r)$ and $S(k)$ of the final configuration. (g) is the fraction of the system in each polymorph, as a function of time. The initial amorphous configuration has 35% of molecules identified as fcc like, 21% hcp-like and 45% bcc-like. This is the configuration number 5 of Table S1, and it crystallises into the fcc polymorph 102 times out of 200, into the bcc polymorph 77 times, and does not crystallise the remaining 21 times. The configuration is available in .xyz format in the supporting information.

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form. Both the polymorph present in the largest amounts, and the bias in the overall crystalline ordering, only predict the correct result a majority of the time. And we cannot make any prediction at all based just on the $S(k)$.

It is worth noting that as most molecules of a given polymorph are in a single large cluster, many of these clusters are big enough to span the system (simulation box). An example of this is shown in Figure S3. When two clusters (typically the fcc and bcc clusters) do so, they form two interpenetrating networks of the two polymorphs. The state then looks analogous to the bicontinuous microemulsion phases found in some mixtures of oil, water and surfactant, and in some mixtures of block copolymers and polymers.[32,33] Here, instead of interpenetrating networks of oil and water, we have networks of polymorphs.
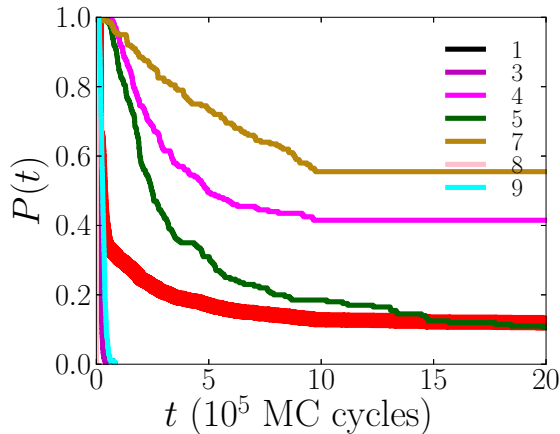

Figure 5: Probability of a realisation of our amorphous state that is amorphous at time $t = 0$ still being amorphous at time t, $P(t)$. The thick red curve is the average over all nine configurations (and so 1800 runs). We have also plotted $P(t)$'s for seven individual configurations, shown as thinner curves. The legend indicates the configuration numbers. Configurations numbers 6 and 10 crystallise almost as soon as they formed, so for these two we have not plotted $P(t)$ curves.

We finish our discussion of the non-equilibrium amorphous state by discussing its stability. In Figure 5 we have plotted the probability, $P(t)$, that a realisation of our non-equilibrium amorphous state remains amorphous after a time t. The probability that it has crystallised after a time t is then $1 - P(t)$.

Also, in Figures 3(g) and 4(g), we have plotted the fractions of molecules in the three polymorphs as a function of time during crystallisation. The amorphous state is often relatively transient in the sense that it crystallises essentially as soon as it forms. However, it can also persist for more than 2 million MC cycles, i.e., neither the bcc nor the fcc polymorph grows to dominate ($> 80\%$) the system for millions of cycle.

There is a very large variation between one configuration and another. For example, configuration number 6 crystallises essentially as soon as it forms, while over half our 200 runs for configuration 7 failed to crystallise after 2 million MC cycles. Note that the time at which a run is said to have crystallised will depend on how we define the crystal; the fractions in the polymorphs and the height of the peaks in $S(k)$ (see Figure S4) vary continuously. However, the variability is so large that by any reasonable measure some realisations of the amorphous state are much longer lived than others.

Although we cannot simulate large volumes, our results suggests that in a large volume in which multiple amorphous domains nucleate and grow, that some would crystallise rapidly while others would grow much larger before crystallising. Thus we would not see a macroscopic domain of the amorphous state, but a mixture of amorphous, crystallising and already crystalline domains.

At the temperature and pressure at which we work, the fcc is the equilibrium state. So, ultimately we expect the bcc crystal to transform to the fcc polymorph. However, this process appears slow. It did not occur in direct simulations. We attempted Forward Flux Sampling (FFS)[30,34] simulations of fcc nucleation from our bcc states, but they were unsuccessful. So although we expect that the bcc phase will ultimately transform into the fcc phase, the bcc phase is clearly stable for long periods.

In summary, in computer simulations of a simple model, we observe an apparently amorphous state. In this state, although almost all the molecules are in locally crystalline environments, there is no long-range crystalline order, and so the $S(k)$ is liquid-like. It is a fascinating open question as to whether this medium-range-crystalline/paracrystalline/nanocrystalline order

is also present in any of: amorphous silicon,[1–3] two-line ferrihydrite,[4–6] metallic glasses,[35] polymers,[36] ACC,[7–16] ACP[17] and ACS.[18–20]

Whether or not these materials have this ordering has consequences. Medium-range crystalline order affects transport properties for electrons and holes, and so understanding this ordering is crucial to device applications.[36] Also, ACC, ACP and ACS are all intermediates in the pathway to crystallisation. If there is medium-range crystalline ordering in these states, then their crystallisation may be closer to a polymorph-to-polymorph conversion than to crystallisation from a liquid.

We have seen that the $S(k)$ is insensitive to the medium-range crystalline order of our state. So, powder X-ray diffraction will fail to detect this ordering, it will not be able to tell liquid-like local structure from crystalline. To distinguish the two, real-space imaging is needed. In our simulations this is trivial as we know exactly where all our molecules are, but imaging single atoms and molecules in experiment is very challenging. However, the resolution of electron microscopy is rapidly improving, and single atoms can now be imaged in three dimensions.[37,38] If this new generation of electron microscopes is used to image states currently considered amorphous, we may well find surprising amounts of local crystalline order.

Supporting Information contains: a description of our simulation methods; definitions of our order parameters, and plots of their values in the states we study; partial $S(k)$'s for individual polymorphs; tabulated data on crystallisation of the amorphous state; the width of the peak in $S(k)$ during crystallisation; analysis of the structure of a larger system; two movies showing rotating animations of the state; two configuration files in .xyz format. The Supporting Information is available free of charge on the ACS Publications website at DOI: TBA.

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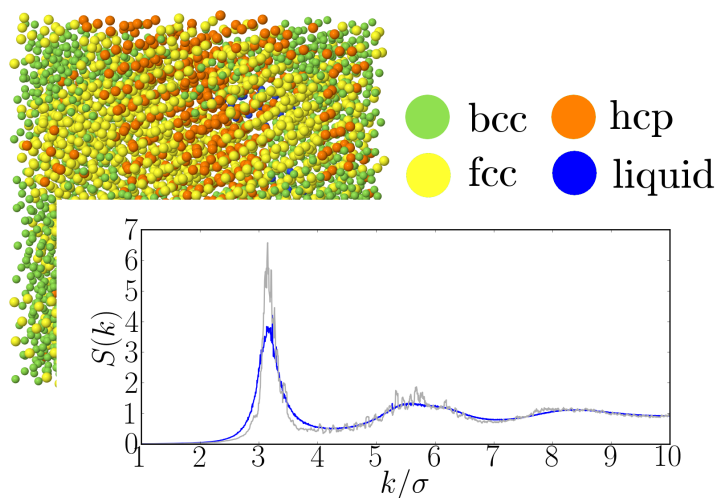
Sixty-word synopsis:

Using computer simulations, we study a non-equilibrium state with a liquid-like $S(k)$ but where over 95% of the molecules are in locally crystalline environments. Due to its liquid-like $S(k)$ and slow dynamics, the state is apparently amorphous, although it contains nanocrystalline order. This nanocrystalline order can strongly bias the polymorph that forms, when the state crystallises.